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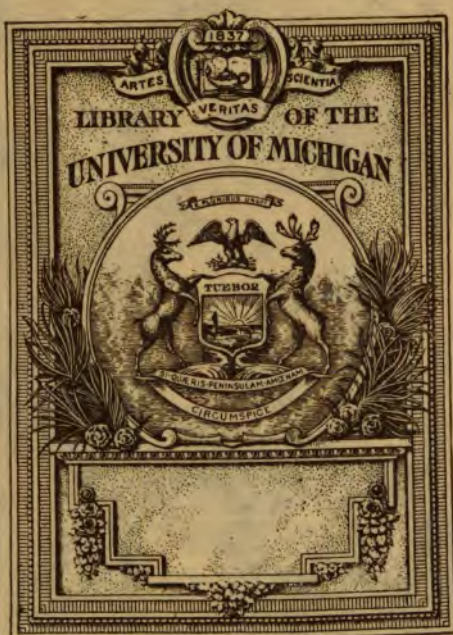
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# **The Reactions of Calcium Carbide with the Vapors of Certain Organic Compounds**

## **A DISSERTATION**

**Submitted to the Faculty of Sciences of the Catholic  
University of America in partial Fulfillment  
of the Requirements for the Degree  
of Doctor of Philosophy.**

**By  
A. J. McGRAIL.**

**Washington, D. C.  
1916.**



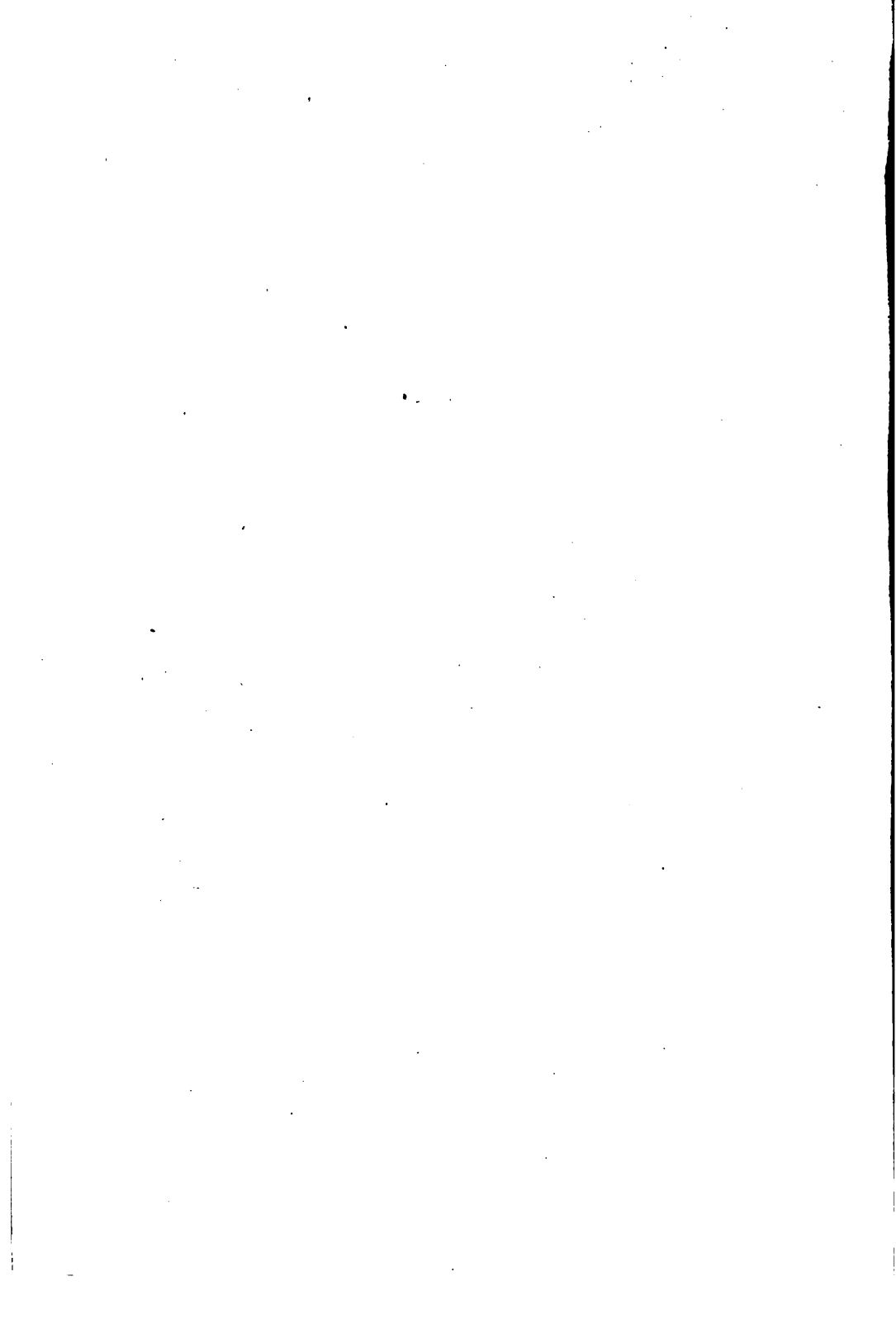
24 May 1865

### ACKNOWLEDGMENT.

This research was undertaken at the suggestion of Dr. John J. Griffin and was carried out under his direction. I wish to express my gratitude to him for his advice and encouragement throughout the progress of this work.

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## SOME REACTIONS OF CALCIUM CARBIDE.

Although the reaction of Calcium Carbide with water has been known for several years, it seems strange that a search of the literature upon the subject reveals the fact that only a few attempts have been made to study the effect of this powerful reagent upon other compounds.

Calcium carbide was used by Hugo Haehn as a condensing agent for organic acids. His method of experimentation was to pass vapors of the various acids over heated carbide. He observed the formation of acetylene and the corresponding ketone. Formic acid was converted into water and carbon monoxide, acetic acid gave acetone and a small amount of methyl alcohol, propionic acid formed diethyl ketone, butyric acid formed dipropyl ketone, isovaleric acid produced valeric aldehyde and valerone, while benzoic acid was converted into benzophenone.<sup>1</sup>

Bodroux and Taboury studied the reaction of calcium carbide on various ketones. Acetone, butanone, and acetophenone condensed to higher boiling compounds, with the elimination of water. Pentanone-3, however, would not react, and the authors concluded that the acetyl group  $\text{CH}_3\text{CO}-$  was essential for the condensation.<sup>2</sup> P. Lefebvre studied this condensation with several substances at  $500^\circ$ . Amyl chloride gave both gaseous and liquid products. The gases consisted of acetylene, ethylene, several other hydrocarbons, and hydrogen. The liquid was a mixture of the amylenes, including methyl-2 butene-1, and methyl-2 butene-2, and the amyl chlorides. The solid products were calcium oxide and calcium chloride.<sup>3</sup>



Lefebvre then extended his researches to the alcohols. Amyl alcohol produced acetylene, ethylene, carbon monoxide,

<sup>1</sup> Haehn, Ber., 39, 1703, (1906).

<sup>2</sup> Bodroux and Taboury, Bull., (4), 3, 831, (1908).

<sup>3</sup> Lefebvre, Compt. Rend., 130, 1036, (1900).

carbon dioxide, ethane, and hydrogen. Ethyl alcohol and methyl alcohol formed gases of similar composition, but from isobutyl alcohol some butylene was derived. In every case he found that the gaseous products consisted of at least 60 per cent hydrogen, a greater percentage than that in the original substances, while the liquid products, consisting chiefly of aldehydes, contained less. Lefebvre's explanation was this, "The formation of the aldehyde results from the dehydrogenation of the alcohol by heat, favored in the presence of the nascent acetylene, by the combination of the latter with hydrogen."<sup>4</sup>

Forcrand heated absolute alcohol in sealed glass tubes with calcium carbide at 180° for many hours.<sup>5</sup> He expected to find calcium ethylate but obtained instead calcium alcoholate, to which he gave the formula  $(\text{CaO})_3(\text{C}_2\text{H}_5\text{OH})_4$ .

Wagner isolated and studied the different products formed in the reaction of calcium carbide on acetone.<sup>6</sup>

The work above described represents about all that has been done upon the reactions of calcium carbide and organic reagents, and it seemed advisable to investigate its reactions as a condensing and catalytic agent for different types of organic compounds. Acetaldehyde was the first substance which was chosen for investigation because of its well-known reactions with several condensing agents.

## THE CONDENSATION REACTIONS OF ACETALDEHYDE.

When an aqueous solution of hydrochloric acid is allowed to react with cold acetaldehyde, a polymer of the latter, oxybutyric aldehyde or aldol, is formed, and the process is called after the latter compound, the aldol condensation. Solutions of zinc chloride, as well as dilute solutions of alkaline salts, such as sodium acetate, potassium acetate, potassium for-

<sup>4</sup> Lefebvre, *Compt. Rend.*, 133, 1221, (1901).

<sup>5</sup> Forcrand, *Compt. Rend.*, 119, 1266, (1894).

<sup>6</sup> Wagner, *Dissertation*, Catholic University of America, (1913). *Chemical Abstracts*, 8, 91, (1914).

mate, and potassium carbonate induce this condensation. Sodium formate and neutral salts like potassium chloride and potassium sulphate will not cause the formation of aldol. When more concentrated solutions are used and when the temperature is raised, each molecule of aldol loses a molecule of water and crotonaldehyde is formed.<sup>7</sup>

Lieben discovered crotonaldehyde when he heated acetaldehyde with a concentrated solution of potassium formate in a sealed tube.<sup>8</sup> Kekulé converted acetaldehyde into crotonaldehyde by the use of zinc chloride and a little water.<sup>9</sup> Lieben and Zeisel heated a mixture of one volume of a concentrated aqueous solution of sodium acetate and ten volumes of acetaldehyde and discovered, in addition to the crotonaldehyde, the formation of a large quantity of higher condensation products, which changed easily into a resinous mass.<sup>10</sup> A footnote in the memoir of these investigators mentions the use of concentrated solutions of manganous chloride, ferrous chloride, zinc sulphate, and alum in effecting the formation of crotonaldehyde. Sodium carbonate and sodium hydroxide formed viscous liquids, which were probably higher condensation products.<sup>11</sup> It is probable also that in these reactions aldol is first formed and that this substance later breaks down into crotonaldehyde and the other condensation products. Greene dropped acetaldehyde upon melted zinc chloride and obtained paraldehyde, crotonaldehyde, ethylene, and propylene. No acetylene was found.<sup>12</sup> Lieben passed dry hydrochloric acid gas into some pure acetaldehyde which was surrounded by a cooling mixture. The gas was absorbed, the volume of the liquid increased, and it separated into two layers, one of which was an aqueous solution of hydrochloric acid, and the other was the condensation product. This was a clear, colorless liquid, boiling at 116°, and its composition

<sup>7</sup> Beilstein, *Organische Chemie*, III Auflage, I, 916.

<sup>8</sup> Lieben, *Ann.*, Supp., I, 117, (1861).

<sup>9</sup> Kekulé, *Ann.*, 162, 96, (1872).

<sup>10</sup> Lieben and Zeisel, *Monats.*, 1, 820, (1880).

<sup>11</sup> Lieben and Zeisel, *Monats.*, 1, 819, (1880).

<sup>12</sup> Greene, *Amer. Chem. Jour.*, 2, 25, (1880).

corresponded to the formula,  $C_4H_5Cl_2O$ . Lieben called it ethylidene oxychloride.<sup>13</sup> Baeyer considered that the hydrochloric acid formed a molecular compound with the aldehyde, that from two of these complex molecules a molecule of water was eliminated, and that the remaining atom of oxygen formed a bridge between the two molecules.<sup>14</sup>

J. Riban treated ether solutions of acetaldehyde with sodium. He obtained hydrogen, aldol, and a new substance, which he described as the anhydride of aldol. When he heated acetaldehyde with zinc dust in a sealed tube, at  $105^\circ$ , he found hydrogen and several condensation products, among which were crotonaldehyde, aldol, and a new substance. This was a mobile, colorless liquid which had an odor like that of mint. It was lighter than water and boiled under ordinary pressure at  $220^\circ$  but in a vacuum at  $140^\circ$ - $150^\circ$ . On repeated distillation it changed, with the elimination of water, into higher boiling compounds. Riban assigned to it the formula,  $C_6H_{10}O_2$ , and believed it to be formed by the condensing of three molecules of acetaldehyde with the elimination of one molecule of water.<sup>15</sup>

Kekulé described the compounds  $C_6H_8O$  and  $C_8H_{10}O$ . These were prepared by heating acetaldehyde with crotonaldehyde in the presence of zinc chloride.<sup>16</sup>

Zeisel and von Bitto heated ten volumes of acetaldehyde with one volume of a saturated aqueous solution of sodium acetate at  $95^\circ$  for 36 hours. They removed the crotonaldehyde, and the products boiling above  $120^\circ$  were distilled with steam. A large portion was not volatile. From the volatile portion they separated by fractional distillation two isomers, which had the composition expressed by the formula,  $C_6H_8O$ , and which showed the properties of an aldehyde with two double bonds. One boiled at  $75^\circ$ - $80^\circ$  under a pressure 24-26 mm. and the other boiled at  $55^\circ$  under the same pressure, but

<sup>13</sup> Lieben, Ann., 106, 336, (1858).

<sup>14</sup> Kekulé, Ann., Supp., V, 79, (1867).

<sup>15</sup> Riban, Jahresbericht, (1872), 433. Bull., 18, 63, (1872).

<sup>16</sup> Kekulé, Ann., 162, 105, (1872).

at 141°-143° under normal pressure. In the fraction, non-volatile in steam, they found a new substance,  $C_{10}H_{14}O_2$ , which contained but one aldehyde group, the other oxygen atom serving as a bridge between the two parts of the compound. This aldehyde boiled at 159°-163° under a pressure of 16.5 mm.<sup>17</sup>

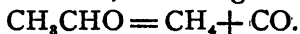
Lieben, as the result of his researches, suggested the following rule for the condensation of aldehydes, "the condensation of two molecules of the same aldehyde, or of different aldehydes, forming one molecule of an unsaturated aldehyde, takes place in such a way that the oxygen atom of one molecule unites with the hydrogen atoms of the  $CH_2$  group, adjacent to the  $CHO$  group of the other molecule, water is eliminated, and the two residues unite to form an unsaturated molecule."<sup>18</sup>

### THE EFFECT OF HEAT UPON ACETALDEHYDE.

The action of heat upon acetaldehyde would naturally effect some reactions independently of the calcium carbide and our present knowledge of the subject is represented by the following facts:

M. Berthelot heated pure acetaldehyde for 100 hours at 160°. No gas was evolved, but water and a resin were formed, together with small amounts of acetic acid and ethyl alcohol.<sup>19</sup>

Bone and Smith vaporized acetaldehyde into a tube, heated to 400°. The aldehyde was at once broken down into methane and carbon monoxide, according to the reaction—



No carbon was found and the gases were present in equal volumes. The reaction thus involves the movement of an atom of hydrogen from one carbon atom to the other. At 600° carbon was found in the tube and the analysis of the gas showed that some of the methane had broken down into hy-

<sup>17</sup> Zeisel and von Bitto, *Monats.*, 29, 591-605, (1908).

<sup>18</sup> Lieben, *Monats.*, 22, 289, (1901).

<sup>19</sup> Berthelot, *Ann.*, 128, 256, (1863).

drogen and carbon. The gas contained 48.7 per cent of carbon monoxide, 45.7 per cent of methane, and 5.6 per cent of hydrogen. At 800° there was found a still greater amount of carbon and hydrogen, while the percentage of methane had diminished. Traces of acetylene were found. The tube was then filled with pieces of porcelain and maintained at 400°-500°. Carbon was deposited in the tube and the distillate separated into two layers, one of which was water, and the other contained unsaturated aldehydes. The quantity of methane fell to 18.7 per cent, and in its place about 14 per cent each of ethylene and ethane were found. The porcelain, probably, acted as a catalyst for the aldol condensation, which, in turn, gave rise to unsaturated aldehydes and water.<sup>20</sup>

The above work upon acetaldehyde is summarized in the following table of condensing agents and products:

Condensing Agent.	Products.
Potassium formate..	Crotonaldehyde... Lieben.
Zinc chloride.....	Crotonaldehyde... Kekulé.
Sodium acetate.....	High boiling substances..... Lieben and Zeisel.
Hydrochloric acid..	Ethylidene oxychloride..... Lieben.
Sodium.....	Aldol, etc..... Riban.
Zinc.....	$C_6H_{10}O_4$ ..... Riban.
Zinc chloride.....	$C_6H_8O$ and $C_8H_{10}O$ ..... Kekulé.
Sodium acetate.....	$C_6H_8O$ and $C_{10}H_{14}O_2$ ..... Zeisel and von Bitto.

At low temperatures acetaldehyde decomposes into carbon monoxide and methane, at higher temperatures some hydrogen is produced, and in the presence of porcelain some ethylene and ethane are formed.

<sup>20</sup> Bone and Smith, J. Chem. Soc., 87, 1, 210. (1905).

## THE REACTION OF ACETALDEHYDE AND CALCIUM CARBIDE.

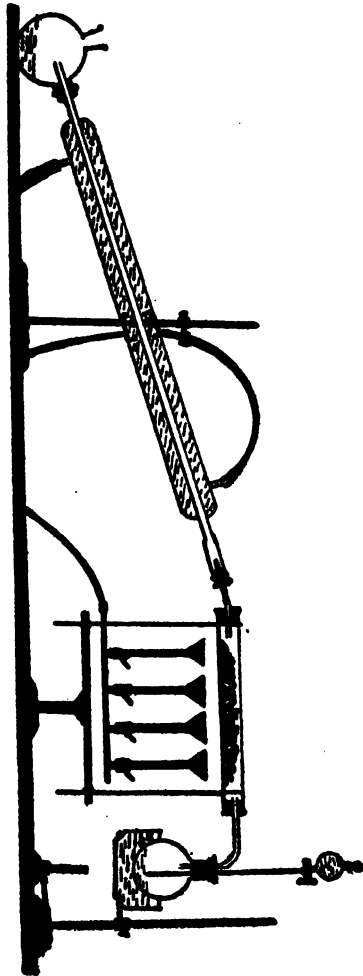
Since the literature contains no account of a reaction of calcium carbide and acetaldehyde, we thought it advisable to find out if a reaction occurred and to learn if the products were different from those obtained when other condensing agents were employed. With this object in view, the following experiments were carried out at ordinary temperatures and at low red heat:

A quantity of clean lumps of calcium carbide, weighing 20 grams, was crushed to a fine powder and mixed with 100 grams of absolute alcohol and 100 grams of acetaldehyde obtained from Merck. The reaction commenced so vigorously that it was necessary to cool the flask by immersing it in cold water. After standing for two days, the acetaldehyde and alcohol had been transformed into a gelatinous yellow liquid, which, on being cooled, solidified to a resin. In a second experiment, without the addition of alcohol, the reaction was more vigorous, the mixture became quite hot, and some gas, probably acetylene, was formed. The resin, formed in this experiment, was soluble in alcohol, ether, and acetic acid. Its solutions absorbed bromine very readily. It is quite probable that this resin is similar to the one found by Weidenbusch, who obtained it by the action of alkalis upon acetaldehyde.<sup>21</sup>

The unsatisfactory nature of this substance, formed at low temperatures, having precluded successful investigation, it was decided to study the reaction at higher temperatures.

A piece of durax glass tubing about 1 meter long was placed in a small combustion furnace and heated to a faint red heat. The tube was drawn down at one end so that it might be attached to a condenser by means of a stopper. The liquid under investigation was placed in a round-bottomed flask upon a water bath, which was heated sufficiently to

<sup>21</sup> Weidenbusch, Ann., 66, 152, (1848).





force a slow stream of vapor into the durax tube, which was filled with well-sifted lumps of calcium carbide. A dropping funnel, closed by a calcium chloride tube, served to replenish the supply of acetaldehyde in the vaporizing flask, and a second round-bottomed flask served as a receiver. This arrangement of apparatus was devised to obviate the cracking of the tube, which always resulted when the acetaldehyde was allowed to flow directly into it.

A vigorous reaction commenced as soon as the vapors came in contact with the heated carbide, dense white fumes appeared, and a dark yellow, fluorescent liquid condensed in the receiver. From this liquid a solid substance would separate at times, only to dissolve again on standing. Uncondensed gases escaped from the apparatus. The carbide changed into a soft, yellowish white powder, in which there was a great deal of carbon. The gaseous mixture was passed through Dreschel bottles containing bromine water in order to remove any unsaturated compounds, and was then analyzed and found to contain the gases listed in the following table:

$\text{CO}_2$	$\text{CO}$	$\text{CH}_4$	$\text{H}_2$
7.4%	7.7%	7.7%	74.8%

A second sample, analyzed for unsaturated compounds only, gave the following results:

$\text{C}_2\text{H}_2$	$\text{C}_2\text{H}_4$
17.1%	13.1%

The yellow liquid was roughly fractionated and these fractions were carefully redistilled with a Vigreux column. Four principal portions were obtained, boiling within the following limits: 33°-36°, 47°-55°, 67°-70°, and 78°-80°. Eighty per cent of the distillate was contained in the last two fractions. On further heating, the contents of the distilling flask commenced to bump and to condense with the elimination of water. As soon as this occurred, the distillation was stopped

and the residual liquid was saved for further study. This portion never amounted to more than 1 or 2 per cent of the total quantity of distillate. The first two fractions were very volatile and consisted chiefly of unchanged acetaldehyde. The third fraction was less volatile, and when fractionated, it passed partly to the lower fraction and partly to fraction IV. All four fractions absorbed bromine readily. As the distillate was evidently a mixture of several compounds, it was hoped to identify them or to effect a separation by the usual laboratory methods.

About 45 grams of the fourth fraction were treated with an excess of bromine water, thus causing the separation of 2 or 3 cubic centimeters of a heavy liquid, which, on account of its small quantity, was not subjected to further investigation. After separating this heavy liquid, the remainder of the sample was placed in a distilling flask and heated on a water bath. When two-thirds of the distillate had come over at 78°-80°, the residue in the flask suddenly condensed to a resin, black in color, and somewhat like rubber in consistency. This resin, however, was insoluble in the usual solvents. A second sample, when brominated with liquid bromine, behaved in a similar manner.

Iodine was shaken up with a portion of fraction IV. The liquid turned to the characteristic brown color of alcoholic solutions of iodine, but otherwise no action was noted. It seems, therefore, plausible to conclude that this fraction contains at least a pair of unsaturated carbon atoms.

Acetyl chloride reacted so vigorously that the test tube had to be cooled to prevent the contents from boiling away. The odor of ethyl acetate was observed and drops of this ester were seen in the mixture.

Ammoniacal solutions of cuprous chloride were without any action, though when concentrated solutions of ammonium hydroxide were added an odor somewhat like that of acetonitrile was noted.

The ordinary tests for an aldehyde were then applied. A mixture of ammonium hydroxide, sodium hydroxide, and sil-

ver nitrate formed only a minute deposit of silver, thus indicating the presence of not more than a trace of aldehyde, and this was confirmed by the fact that a dilute solution of fuch-sine, which had been bleached by sulphur dioxide, developed only a very faint pink color, when this reagent was added to a test sample of the liquid. This color persisted for a very few minutes. Ten cubic centimeters of fraction IV were shaken up with an equal volume of a saturated solution of sodium bisulphite without forming any addition compound.

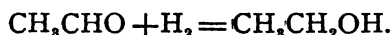
To 5 grams of fraction IV an equal quantity of hydroxyl-amine hydrochloride was added in the cold. The free acid was then neutralized with sodium carbonate, and a slight turbidity, which had been noted, cleared up after neutralization. The solution was allowed to evaporate in the air but crystals did not form for several days. The solid residue was extracted with 98 per cent alcohol, and the light yellow solution was allowed to evaporate. A crop of yellow hexagonal crystals was obtained. On attempting to recrystallize these from various solvents such as benzol, ether, chloroform, and water, an amorphous, yellow paste resulted. This substance charred, when heated to 120°, but did not melt, and it gave off a nitro-genous odor. Two other unsuccessful attempts were made to obtain the hexagonal crystals. These crystals are not necessarily evidence for the presence of an aldehyde in frac-tion IV, for hydroxylamine has also the power of saturating a double bond.<sup>22</sup> In this case one hydrogen atom adds to one carbon atom, and the residue, —NHOH, goes to the other carbon atom.

The boiling point of the fraction and the reaction with acetyl chloride indicated that ethyl alcohol was present. This point was proved by the formation of ethyl benzoate. Ten grams of benzoic acid were heated under a reflex condenser on a water bath with 20 grams of fraction IV, which had been saturated with dry hydrochloric acid gas. After half an hour the mixture had darkened; then the reflux was re-

<sup>22</sup> Weyl, *Methoden Org., Chem.*, II, 643, (1910).

placed by a side condenser and no distillate was obtained at the temperature of the water bath. The mixture was diluted with twice its volume of water and sodium carbonate was added to neutralize the acid. An oil, which rose to the surface, was separated in a separatory funnel and dried over fused calcium chloride. This distilled as a clear, yellow, pleasant-smelling liquid at  $210^{\circ}$ - $215^{\circ}$ , a fair boiling point for ethyl benzoate made under such conditions.

The formation of alcohol can be explained by the assumption that the acetylene, formed by the action of the calcium carbide upon the acetaldehyde, decomposes at once into carbon and hydrogen, and the nascent hydrogen of this decomposition reaction effects the reduction of another molecule of acetaldehyde to alcohol.



Fraction IV consisted chiefly of a constant boiling mixture of ethyl alcohol and some other compound which contains a double bond. The tests for aldehydes showed that there was no more than a trace of these substances in the fraction and the failure of the cuprous chloride to react proved the absence of acetylene in solution.

The following attempts were made to identify the higher boiling compounds and to avoid the process of distillation, which always resulted in a continued condensation.

Clemmensen's method had been applied to such a variety of compounds that it seemed as if it might be successful in reducing the oil.<sup>23</sup> Fifteen grams of fine zinc dust were amalgamated by a 5 per cent solution of mercuric chloride. After an hour the zinc-mercury couple was well washed with water and placed in a small, round-bottomed flask, attached to a reflux condenser. Then 10 cubic centimeters of undistilled liquid and 150 cubic centimeters of concentrated hydrochloric acid were poured upon the zinc-mercury couple, and the mixture was heated for many hours without any reduction being effected.

<sup>23</sup> Clemmensen, Ber., 46, 1387, (1913).

Doby's reaction was tried upon a second portion of the unfractionated liquid.<sup>24</sup> This method depends upon the powerful reducing action of absolute alcohol, saturated with dry ammonia, and metallic calcium. Thirty cubic centimeters of absolute alcohol were saturated with ammonia, and 3 cubic centimeters of liquid and 1 gram of finely cut chips of calcium were added to the alcohol. This mixture was allowed to stand for some days, during which time an occasional bubble of hydrogen was noticed, but the oil was unchanged. A second experiment was performed with the same quantities of liquid and calcium, but with alcohol which had not been treated with ammonia. After two days a steady stream of hydrogen bubbles came from the mixture, the calcium turned white, and an aldehyde resin was formed. Since this method of attacking the problem proved to be unsuccessful, it was decided to reserve this point for future study.

The Reaction Products.—When cold acetaldehyde is mixed with calcium carbide, a resin is formed. When the vapors of acetaldehyde are passed over hot calcium carbide, the following products are obtained: Carbon, calcium oxide, ethyl alcohol, and some unsaturated substance which is volatile with alcohol, carbon dioxide, carbon monoxide, acetylene, ethylene, methane, and a great amount of hydrogen.

### THE REACTION OF ACETAMIDE WITH CALCIUM CARBIDE.

In connection with the investigation of the reactions of calcium carbide, in progress in this laboratory for several years, it was decided to make a study of the action of calcium carbide in removing the elements of water from various types of compounds. A substance most favorable for this study was acetamide, because its reactions with different dehydrating agents have been well worked out.

Acetonitrile was discovered by Dumas in 1848 as the chief

<sup>24</sup> Doby, *Zeit., anorg., Chem.*, 35, 93, (1903).

product of the reaction of phosphorus pentoxide on acetamide.<sup>25</sup> Henke, using rather impure materials, found that the reaction between phosphorus pentachloride and acetamide was so energetic that he had to add an equal volume of sand, in order to slow down the process.<sup>26</sup> He obtained acetonitrile. Wallach repeated this work with pure materials. Dry acetamide and phosphorus pentachloride did not react when cold, but the reaction took place when the mixture was heated. Acetonitrile was obtained in a very impure condition, for it was mixed with phosphorus trichloride and phosphorus oxychloride.<sup>27</sup> Louis Henry used phosphorus pentasulphide. He obtained about one-half of the theoretical yield of nitrile, but the substance smelled strongly of hydrogen sulphide.<sup>28</sup>

Demarçay heated acetamide with a small amount of glacial acetic acid in a flask connected by a Le Bel-Henninger column to a condenser. The reaction ran very smoothly and the nitrile was quite pure.<sup>29</sup> Franchimont employed acetic anhydride for the same purpose, and he succeeded also in obtaining the nitrile by the use of a mixture of acetic anhydride and sodium acetate.<sup>30</sup>

Seifert heated acetamide, absolute alcohol, and sodium in a sealed glass tube at 170°-200°. Much gas, smelling strongly of ammonia, was found. The chief product, however, was ethylamine.<sup>31</sup>

Michaelis and Siebert added to a mixture of 5 grams of acetamide and 50 grams of benzol 10 grams of thionyl chloride, and a white crystalline precipitate formed at once. On heating the mixture on the water bath, complete solution took place, sulphur dioxide and hydrochloric acid were given off, and the distillate responded to the reactions of acetonitrile. They obtained similar results, without the addition of

<sup>25</sup> Dumas, *Ann.*, 64, 333, (1848).

<sup>26</sup> Henke, *Ann.*, 106, 273, (1858).

<sup>27</sup> Wallach, *Ann.*, 184, 22, (1877).

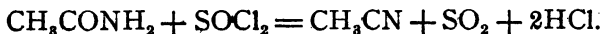
<sup>28</sup> Henry, *Ann.*, 152, 149, (1869).

<sup>29</sup> Demarçay, *Bull.*, 33, 457, (1880).

<sup>30</sup> Franchimont, *Rec., trav. chim.*, 2, 344, (1884).

<sup>31</sup> Seifert, *Ber.*, 16, 1357, (1885).

benzol, but this required heating for eight hours under a reflux condenser.<sup>32</sup>



Most dehydrating agents lead to the formation of acetonitrile, which frequently contains impurities, formed in the side reactions, but sodium and alcohol form ethylamine from acetamide.

With the object of finding a new method for the preparation of acetonitrile we carried out the following experiments upon the reaction of calcium carbide and acetamide:

Clean lumps of calcium carbide were ground to a fine powder, of which 30 grams were taken for the experiment and mixed with 20 grams of dry acetamide. This mixture was placed in a retort, warmed for a few minutes, and then distilled. The distillate was a clear, yellow liquid, boiling at 81°-83°. Eleven grams of this distillate, amounting to 80 per cent of the theoretical yield, were obtained in one experiment. Acetylene was formed during the reaction; the gas had an odor like ammonia and was alkaline in reaction to litmus. No attempts were made to analyze it.

The reaction between calcium carbide and acetamide runs very smoothly and affords an excellent method for the preparation of acetonitrile.

### THE REACTION OF ACETANILIDE WITH CALCIUM CARBIDE.

Acetanilide was considered to be a suitable substance for investigation, for in this case both aniline and a nitrile might be expected as products of the reaction.

Brakebusch reported the formation of nitrile of toluol by heating acetanilide with hydrochloric acid.<sup>33</sup> Jackson doubted the accuracy of this observation and so he repeated the work using hydrochloric acid and, in addition, calcium chloride and

<sup>32</sup> Michaelis and Siebert, *Ann.*, 274, 312, (1893).

<sup>33</sup> Brakebusch, *Dissertation*, Goettingen, (1873).

zinc chloride, but he could not confirm Brakebusch's results.<sup>34</sup> Nietzki decomposed acetanilide by vaporizing it into a red hot tube and obtained benzol, aniline, hydrocyanic acid, and diphenyl urea. The decomposition of acetanilide into diphenyl urea should lead to the formation of acetone, but no acetone was found.<sup>35</sup> Rudolph observed that at a temperature of 250°-270° a reaction took place between zinc chloride and acetanilide from which water was eliminated and a new substance was formed. This was a bright yellow dyestuff, which he called flavaniline, and to which he assigned the formula  $C_{16}H_{14}N_2$ .<sup>36</sup> Acetanilide, when hydrolyzed by boiling with strong solutions of the alkalies, hydrochloric acid, and moderately strong sulphuric acid, is converted into aniline and acetic acid. These are the most important of the reactions of acetanilide.

Our experiments were carried out according to the method which we employed in the study of acetamide.

A mixture of 60 grams of finely crushed calcium carbide and 50 grams of acetanilide was placed in a glass retort and warmed. After 10 minutes the temperature of the retort was gradually raised until a distillate came over, then the temperature was held quite constant. Dense white fumes, alkaline in reaction, appeared in the condenser; this gas reacted very quickly with ammoniacal solutions of silver nitrate forming a precipitate of silver acetylide. The distillate was dark brown in color and the residue in the retort contained much carbon.

When analyzed, the gaseous mixture was found to contain acetylene, carbon monoxide, ethylene, methane, and hydrogen.

<sup>34</sup> Jackson, Ber., 8, 1171, (1875).

<sup>35</sup> Nietzki, Ber., 10, 476, (1877).

<sup>36</sup> Rudolph, Ber., 15, 1500, (1882).



## Analyses of the Gas.

	I	II
$C_3H_2$ .....	12.0	12.0
$C_2H_4$ .....	5.5	7.0
CO .....	3.9	3.3
$H_2$ .....	20.4	17.1
$CH_4$ .....	38.5	30.8

The distillate weighed 29 grams. This was fractionated and at 80° a few drops of liquid distilled over. The temperature rose at once to 180°-184° and remained at this point until the end of the distillation. The first fraction was so small that no tests could be applied to determine its nature, but its boiling point was sufficient to indicate that it was benzol. The second fraction, after another distillation, was a bright yellow oil, boiling at 182°, which had all the characteristic reactions of aniline. It weighed 25 grams. Two other experiments with smaller amounts of reagents confirmed all of these results.

The products of the reaction of acetanilide with calcium carbide are acetylene, ethylene, carbon monoxide, hydrogen, carbon, traces of benzol, and aniline. No acetone and no diphenyl urea were found. Water is probably formed by the union of an oxygen atom from the acetyl group with hydrogen atoms from the same group. This view is supported by the presence of ethylene in the gaseous mixture. The temperature of the retort was hardly sufficient to decompose either acetylene or benzol, hence it seems reasonable to suppose that the hydrogen results from the decomposition of the acetyl group. This reaction, however, is so complex that it is impossible to represent it by simple equations.

### THE REACTION OF ETHYL ACETATE WITH CALCIUM CARBIDE.

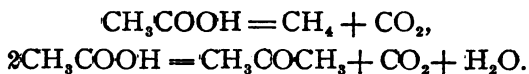
Our next step was to investigate the reaction of calcium carbide with various esters, for we wished to learn how the

elements of water might be eliminated and the esters seemed especially suitable for investigation because the hydrogen, necessary for the formation of water, might be obtained either from the acidic part or the alcoholic part of the compound. This study was made with ethyl acetate, ethyl oxalate, and ethyl salicylate, because they represent different classes of esters and no reactions were known to take place between them and calcium carbide.

Oppenheim and Precht vaporized ethyl acetate into an iron tube, heated to a temperature somewhat under red heat. They found that the ester had decomposed into acetic acid and ethylene, according to the following equation:



Upon raising the temperature to dark red heat, they found carbon dioxide, ethylene, methane, and acetone.<sup>37</sup> They assumed that these substances were decomposition products of acetic acid and that the acid was capable of undergoing decomposition in two different directions, according to these equations:



Liubawin heated ethyl acetate with lime in a sealed tube. At 200° the ester was completely absorbed, forming, probably, calcium acetate and calcium ethylate. At 250° this mixture decomposed into calcium butyrate.<sup>38</sup>

H. Jahn vaporized ethyl acetate over zinc dust, placed in a narrow glass tube in a combustion furnace. The distillate proved to be acetone, and the gases, after the removal of the carbon dioxide, consisted of 53.4 per cent of hydrogen, 28 per cent of ethylene, and 18.6 per cent of carbon monoxide.<sup>39</sup> This brief account summarizes the work which has been done on ethyl acetate.

<sup>37</sup> Oppenheim and Precht, *Ber.*, 9, 325, (1876).

<sup>38</sup> Liubawin, *Jahresbericht*, (1880), 787.

<sup>39</sup> Jahn, *Monats.*, 1, 698, (1880).

Thus far no reaction of ethyl acetate in the presence of a contact agent has been observed at temperatures as low as the boiling point. The first experiments with calcium carbide were carried out to determine if a reaction took place in the presence of this reagent at that temperature.

Dry ethyl acetate was boiled for several days under a reflux condenser with lumps of calcium carbide, but no reaction was noted, for the carbide was not affected and the ester was distilled off unchanged. Since no reaction was found to take place at the boiling point of ethyl acetate, it was determined to repeat the experiment at higher temperatures, and for this purpose the apparatus, already described in the report of the work on acetaldehyde, was used. Freshly distilled ethyl acetate was used in each experiment. The distillate was yellow in color and quite fluorescent. Much gas was evolved, and the residue in the combustion tube was a mixture of calcium oxide, calcium carbonate and carbon. The liquid in the receiver was separated into the following fractions:

I.—59°-70°.  
II.—71°-74°.

III.—74°-79°.  
IV.—80°-...

Fraction I was a mixture of acetone and ethyl alcohol, giving the nitroprusside reaction for acetone,<sup>40</sup> and the reactions for ethyl alcohol with phosphorus trichloride and with acetyl chloride. A portion of this fraction was converted into ethyl iodide by means of red phosphorus and iodine. The alcohol and acetone were washed out with dilute solutions of ammonium hydroxide, leaving a residue which proved to be unchanged ethyl acetate.

Fraction II was but slightly soluble in water. It proved to be ethyl acetate mixed with a small amount of alcohol. On treating a portion of this fraction in the cold with acetyl chloride, and on removing the excess of this reagent, it yielded practically pure ethyl acetate.

Fraction III was treated with benzoyl chloride in the cold.

<sup>40</sup> Legal, *Zeit. anal. Chem.*, 24, 148, (1885).

Some unchanged ethyl acetate distilled at 77°-78°, then the temperature rose to 198°, when the excess of benzoyl chloride came over, and at 213° ethyl benzoate distilled. This was followed by the appearance in the condenser of a solid substance, which, after crystallization from alcohol, proved to be benzoic acid, formed, probably, by the decomposition of some ethyl benzoate. The third fraction also consisted of ethyl alcohol and ethyl acetate.

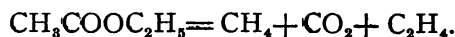
Fraction IV consisted of the residues of all material boiling above 80°. It was separated into two fractions boiling at 125°-130°, and at 190°, respectively. The former was mesityl oxide,  $C_6H_{10}O$ , and the latter was isophorone,  $C_9H_{14}O$ . These are condensation products of acetone which Wagner found in the reaction of calcium carbide and acetone.

The liquid products of the reaction of ethyl acetate with calcium carbide are ethyl alcohol, acetone, mesityl oxide, and isophorone.

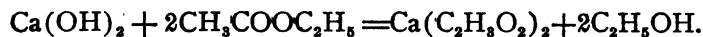
A great amount of trouble was met in securing samples of gas which were free from nitrogen. In the two analyses, listed here, about 24 per cent was inert gas.

	I.	II.
	Per cent.	Per cent.
$CO_2$ .....	20.0	19.3
$C_2H_2$ .....	5.1	4.7
$C_2H_4$ .....	23.2	22.3
$CH_4$ .....	28.2	29.0

The composition of the gaseous mixture, consisting of almost equal volumes of carbon dioxide, ethylene, and methane, indicates that in the presence of calcium carbide one reaction proceeds as follows:



Commercial calcium carbide contains calcium oxide, and its surface is covered by a layer of calcium hydroxide. It is quite probable that this calcium hydroxide decomposes ethyl acetate into calcium acetate and alcohol.



At the temperature of the furnace calcium acetate easily de-

composes into acetone and calcium carbonate and from the acetone made in this reaction mesityl oxide and isophorone are derived.



Ethylene, in addition to its formation in the thermal decomposition of ethyl acetate, may be formed by the reaction of ethyl alcohol with calcium carbide. This reaction will be discussed in another part of this paper. Acetylene may be formed from water, resulting from the condensation of acetone in the presence of calcium carbide, or in the reaction of alcohol and calcium carbide.

At high temperatures ethyl acetate reacts with calcium carbide to form carbon, calcium oxide, calcium carbonate, carbon dioxide, acetylene, ethylene, methane, alcohol, acetone, mesityl oxide, and isophorone.

### THE REACTION OF CALCIUM CARBIDE WITH ETHYL OXALATE.

Ethyl oxalate was prepared according to the method devised by Fittig.<sup>41</sup> A mixture of three parts of anhydrous oxalic acid and two parts of absolute alcohol was heated in a round-bottomed flask, placed in an oil bath. This flask was closed by a stopper provided with two tubes, one of which was connected to a condenser and the other extended from the bottom of the flask to a second flask, which contained two parts of absolute alcohol. As the temperature of the first flask was gradually raised to 125°, alcohol was distilled in from the second flask. The mixture was distilled and the portion coming over above 170° was fractionated, and a pure product, boiling above 183°, was obtained.

A mixture of 45 grams of ethyl oxalate and 15 grams of calcium carbide was kept boiling under a reflux condenser for two days. No reaction took place, for the ester was recovered and the carbide was unchanged.

<sup>41</sup> Fittig, Grundriss Org. Chem., XI Auflage, 253.

The apparatus, already described in the experiments on acetaldehyde, was set up, and ethyl oxalate was vaporized over the hot carbide. This distillate also was yellow and fluorescent, and dense white fumes frequently came through the condenser. Hardly any lime was formed from the carbide but everywhere it was covered with a layer of carbon.

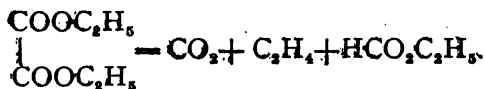
The distillate was fractionated, the first portion coming over between 60° and 85°, then the temperature rose at once to 183° and remained at this point until all the liquid had distilled. A quantity of the lower boiling fraction was then submitted to further fractionation. The first fraction boiled at 54°-56°, the second at 59°-65°, and the third at 78°-80°. The first fraction was quite pure ethyl formate, the second fraction was a mixture of ethyl formate and alcohol, and the third fraction was ethyl alcohol. No other liquid products were found.

Four analyses of the gas were made.

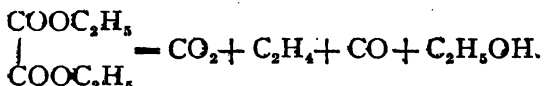
CO <sub>2</sub> .....	27.71	27.67	41.08	39.81
C <sub>2</sub> H <sub>2</sub> .....	2.67	2.36	4.74	2.50
C <sub>2</sub> H <sub>4</sub> .....	32.73	33.85	23.60	26.44
CO .....	12.34	16.20	9.60	11.61
C <sub>2</sub> H <sub>6</sub> .....	....	....	6.7	3.9

In the first two analyses the residues, when mixed with air and ignited, exploded, and water and carbon dioxide were formed, but it was impossible to determine from the results the composition of the gas. In the third and fourth analyses the contractions, and the absorptions in potassium hydroxide corresponded quite closely with those calculated for ethane.

The small quantity of acetylene is notable, for it shows that the calcium carbide, in this reaction, does not tend to remove the elements of water from ethyl oxalate. Its action, then, must be catalytic, for it probably causes the breaking down of an ethyl group into ethylene and hydrogen. The hydrogen passes over to the carbon atom of the opposite carboxyl, thus forming ethyl formate. From this reaction we should obtain carbon dioxide, ethylene, and ethyl formate. All these products were found.



The alcohol may be formed by the wandering of a hydrogen atom from one ethyl group to the opposite ethoxy group, and at the same time the reaction should result in the formation of one molecule each of carbon monoxide, carbon dioxide, and ethylene.



The liquid products of the reaction of calcium carbide and ethyl oxalate are ethyl formate and ethyl alcohol. The gaseous products are carbon dioxide, carbon monoxide, ethylene, and a small amount of acetylene. Lorin has reported the formation of ethyl formate and carbon dioxide by heating a mixture of anhydrous oxalic acid and ethyl oxalate.<sup>42</sup>

### THE REACTION OF ETHYL SALICYLATE AND CALCIUM CARBIDE

Baly warmed ethyl salicylate with barium oxide and then heated the mixture to boiling. Barium carbonate was formed and phenetol distilled from the mixture.<sup>43</sup>



No attempts were made to study the reaction of calcium carbide and ethyl salicylate at the boiling point of the latter compound, for this temperature is quite high, so the ethyl salicylate was vaporized over hot carbide in the apparatus already described.

After the reaction, the tube contained some carbon and crystals of salicylic acid.

The distillate was yellow, and, when fractionated, was found to contain not more than a trace of alcohol, but was chiefly a mixture of phenol and unchanged ethyl salicylate.

<sup>42</sup> Lorin, Bull., 49, 345, (1888).

<sup>43</sup> Baly, Ann., 70, 209, (1849).

The phenol was identified by its color reactions with ferric chloride and by conversion into tribromphenol. Twenty cubic centimeters of the distillate were shaken up with water and the ester was separated in a separatory funnel. The water solution was not quite saturated with bromine water and the yellow precipitate was boiled alcohol in order to decompose any tribrom phenol. Water was added to precipitate the tribromphenol, which was then crystallized from chloroform. It melted at  $91^{\circ}$ . No phenetol was found.

In the first two gas analyses the residues, which were very small, did not explode upon ignition. The third residue exploded and the results indicated that the gas contained ethane,

#### Gas Analyses.

CO <sub>2</sub> .....	46.2	45.1	42.2
C <sub>2</sub> H <sub>2</sub> .....	11.2	12.1	11.2
C <sub>2</sub> H <sub>4</sub> .....	30.8	30.2	32.6
C <sub>2</sub> H <sub>6</sub> .....	...	...	4.4

In the reactions of ethyl acetate and of ethyl oxalate with calcium carbide, alcohol was found in considerable amount, but very little alcohol was found in the case of ethyl salicylate. This may be explained by assuming that the reaction runs to form ethylene and phenetol. However, no phenetol was found, but Bamberger has shown that phenetol, when heated to  $380^{\circ}$ - $400^{\circ}$ , breaks down into phenol and ethylene.<sup>44</sup>



The products of this reaction, then, are salicylic acid, phenol, carbon dioxide, acetylene, ethylene, and ethane.

#### THE REACTIONS OF ETHYL ALCOHOL WITH CONDENSING AND CATALYTIC AGENTS.

The importance of studying the reaction of calcium carbide and ethyl alcohol was impressed upon us by the fact that al-

<sup>44</sup> Bamberger, Ber., 19, 1820, (1886).



cohol is a product of the reaction of calcium carbide with acetaldehyde, ethyl acetate, and ethyl oxalate, and is formed to a slight extent in the reaction of ethyl salicylate. If any reaction took place between calcium carbide and alcohol, a knowledge of the reaction products might be useful in aiding us to understand the reactions of calcium carbide with the above-mentioned substances. Ethyl alcohol is a substance capable of reacting in the presence of contact and condensing agents in a variety of ways, and that this fact was noted at quite an early date is shown by the abundant literature upon the subject. The following is an account of some of the work of other investigators.

Basil Valentine, in his work, *The Triumphal Car of Antimony*, describes the preparation, by the distillation of antimonious chloride and ethyl alcohol, of a substance to which he attributed wonderful properties as a medicament.<sup>45</sup> Valerius Cordus is said to have discovered ether by the reaction of ethyl alcohol and sulphuric acid about the year 1540.<sup>46</sup> The explanation of this reaction was the cause of much dispute between the advocates of the various type, radical, and substitution theories during the early decades of the nineteenth century, and was definitely given by Williamson in a research published in 1852.<sup>47</sup>

Baron de Bormes prepared ether by heating alcohol with zinc chloride in a sealed tube of iron. He found also two products which he called sweet oils.<sup>48</sup> This research was soon forgotten, but Masson repeated this work and separated the sweet oils into two fractions. The first fraction boiled below 100°; it was colorless, had a pleasant odor, and was insoluble in water. Its analysis indicated a formula of  $C_6H_8$ . The non-volatile oil was pale yellow and insoluble in water. Masson assigned to it the formula  $C_8H_7$ .<sup>49</sup>

<sup>45</sup> Cf. Kuhlmann, *Ann.*, 33, 98, (1840).

<sup>46</sup> J. B. Cohen, *Organic Chemistry for Advanced Students*, 42.

<sup>47</sup> Williamson, *Quart. J. Chem. Soc.*, 4, 238, (1852).

<sup>48</sup> Cf. Masson, *Ann. chim. phys.*, 69, 238, (1838).

<sup>49</sup> Masson, *Ann.*, 31, 63, (1839).

Boullay substituted arsenic acid for sulphuric acid and showed that ether was the principal product. The purity of his acid was questioned by Thénard and Vauquelin, but, on repeating with pure arsenic acid, free from sulphuric acid, the same result was obtained.<sup>50</sup>

Gay-Lussac and Thénard found that an ether was formed by the reaction of fluorboron on alcohol.<sup>51</sup> This ether was shown by Desfosses to be identical with sulphuric ether. Desfosses found as by-products of the reaction boric acid and hydrofluorboric acid.<sup>52</sup>

Lassaigne distilled alcohol with phosphoric acid. He found ether and a new acid, which he called phosphorvinic acid from its analogy with sulphovinic acid.<sup>53</sup> A note in the *Annales de Chimie*, signed with the initials G.-L. (Gay-Lussac), described a reaction between alcohol and chromic acid.<sup>54</sup> The products of this reaction were ether and the sweet oil previously described by Masson.

Liebig mentioned the use of stannic chloride<sup>55</sup> and Kuhlmann, using this reagent, obtained ethyl chloride and ether. He then studied the effects produced by distilling alcohol with many chlorides. When alcohol and ferric chloride were used in molecular proportions, ethyl chloride was formed, but, on doubling the concentration of the alcohol, ether was formed. Antimonic chloride produced ethyl chloride and a small amount of ether. Aluminic chloride formed ethyl chloride and arsenic chloride did not react at all.<sup>56</sup>

Berthelot heated alcohol and ammonium chloride in a sealed tube. Ether was formed at 200°, but at 400° two layers appeared in the tube, one of water and the other of ether. The aqueous solution contained hydrochlorides of various amines. The reaction was completed at 300° when ammonium iodide

<sup>50</sup> Boullay, *Ann. chim. phys.*, (1), 78, 284, (1811).

<sup>51</sup> Gay-Lussac and Thénard, *Recherches Physico-Chimiques*, II, 39.

<sup>52</sup> Desfosses, *Ann. chim. phys.*, (2), 16, 72, (1821).

<sup>53</sup> Lassaigne, *Ann. chim. phys.*, (2), 13, 294, (1820).

<sup>54</sup> *Ann. chim. phys.*, (2), 16, 105, (1821).

<sup>55</sup> Liebig, *Ann., chim. phys.*, (2), 55, 181, (1833).

<sup>56</sup> Kuhlmann, *Ann.*, 33, 97 and 192, (1840).

was used instead of ammonium chloride.<sup>57</sup>

Greene decomposed alcohol by means of hot zinc chloride. Some hydrochloric acid was set free and the other products were water, a small amount of ether, liquid hydrocarbons, ethylene, hydrogen, a trace of ethane, and much acetaldehyde.<sup>58</sup>

Reynoso mentioned many other earlier works on this question and, in addition, describes his own experiments with chlorides, sulphates, and alums.<sup>59</sup>

According to Meyer and Jacobson the vapor of alcohol is stable at 300°,<sup>60</sup> but Berthelot states that this temperature is too low, and that alcohol does not break down at temperatures below 500°, <sup>61</sup> and Ipatiew has placed the temperature at 700°. <sup>62</sup> Theodore de Saussure passed the vapor of alcohol through a tube of porcelain, heated till it was glowing. The alcohol broke down completely into hydrogen, methane, and carbon monoxide. He found some volatile crystals in his condenser.<sup>63</sup>

Marchand vaporized alcohol into a porcelain tube filled with pieces of glass.<sup>64</sup> It had been thought that alcohol might be readily converted into ether and water at about 120°. Marchand found no reaction at this temperature, but upon raising the temperature to dark red heat, acetaldehyde, hydrocarbons, and water were formed.

Berthelot allowed alcohol to flow into a red hot porcelain tube, filled with pieces of pumice stone. He found naphthalene, which had been found in a similar reaction by Saussure and by Priestley, benzol, phenol, acetaldehyde, and a trace of acetic acid. The gases were hydrogen, methane, and carbon monoxide.<sup>65</sup>

<sup>57</sup> Berthelot, *Ann.*, 83, 107, (1852).

<sup>58</sup> Greene, *Amer. Chem. Jour.*, 2, 23, (1880).

<sup>59</sup> Reynoso, *Ann. chim. phys.*, (3), 48, 428 and 451, (1856).

<sup>60</sup> Meyer and Jacobson, *Lehrbuch der Organischen Chemie*, I, 1, 233.

<sup>61</sup> Berthelot, *Trait de Chimie Organique*, 164, (1872).

<sup>62</sup> Ipatiew, *Ber.*, 34, 598, (1901).

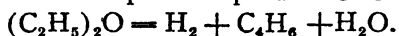
<sup>63</sup> Saussure, *Ann. chim. phys.*, (1), 89, 273, (1814).

<sup>64</sup> Marchand, *J. prak. Chem.*, (1), 15, 7, (1838).

<sup>65</sup> Berthelot, *Ann.*, 81, 108, (1852).

H. Jahn distilled absolute alcohol into a combustion tube, filled with zinc dust, and heated to dark red heat. No liquid products were found, but the gaseous products consisted of methane, carbon monoxide, and hydrogen. At low temperatures the alcohol decomposed quite easily into ethylene, water, and small amounts of acetylene.<sup>66</sup>

Ipatiew subjected the reactions of alcohol in the presence of contact agents to a series of very thorough researches, in which he studied the effects produced by changes in temperature in the contact agent and in the material of the tube itself.<sup>67</sup> Alcohol, when passed through a glass tube heated at 700°, decomposed to a very slight extent, with the formation of a small amount of acetaldehyde. In an empty iron tube the reaction was quite brisk between the limits of 710° and 750°, acetaldehyde, paraldehyde, water, and carbon being formed. Ipatiew continued this work with tubes of glass, porcelain, iron, copper, and platinum, filled with various catalysts, such as zinc, brass, graphite, and the oxides of lead, copper, zinc, nickel, and aluminium. He developed an apparatus for studying these reactions at high pressures, but his products, except in two cases, were always similar to those found by other investigators. In the presence of aluminium and aluminic oxide he obtained some divinyl, which he considered to be a decomposition product of ether.<sup>68</sup>



Ipatiew believed that an oxide was formed by the reaction of the steam in the gaseous products upon the metallic catalyst. This thin film of oxide served to oxidize a molecule of alcohol to aldehyde and was thereby reduced to the metal, which could be oxidized again and thus its catalytic power was restored.<sup>69</sup> He thought that the methane and carbon

<sup>66</sup> Jahn, Monats, 1, 388, (1880).

<sup>67</sup> Ipatiew, Ber., 34, 596 and 3579, (1901).

35, 1047 and 1057, (1902).

36, 1990, (1903).

37, 2961 and 2986, (1904).

Cf. Ehrenfeld, J. prak. Chem., 67, 59, (1903).

<sup>68</sup> Ber., 37, 2990, (1904).

<sup>69</sup> Ber., 34, 3588, (1901).

monoxide, usually found in these reactions, were not derived from the alcohol, but were products of the decomposition of acetaldehyde.<sup>70</sup>

Sabatier and Senderens undertook the study of the reactions of alcohol with the object of finding the lowest temperatures at which the reaction would run, so that they might prevent the decomposition of alcohol into carbon, hydrogen, and hydrocarbons, which were always formed at high temperatures. In the presence of finely divided copper, heated to 250°, alcohol decomposed easily and completely into acetaldehyde, according to the equation—



Nickel at 178° and cobalt and platinum black at slightly higher temperatures induced the same reaction, but when nickel was used the temperature required careful control, for at 230° certain side reactions were catalyzed. They attributed the catalytic power of the metals to the formation of an unstable metallic hydride, which easily decomposed, and which was constantly formed at the expense of the alcohol.<sup>71</sup>

Senderens continued the work and studied the catalytic effects of animal charcoal,<sup>72</sup> red phosphorus,<sup>73</sup> and amorphous and crystalline alumina and silica.<sup>74</sup> He observed that the method of preparation and the character of the catalyst influenced considerably the temperature of decomposition and the course of the reaction. Amorphous silica and alumina, moderately heated, catalyze the formation of ethylene and water. If the catalysts were previously ignited in a muffle, the alcohol tended to break down into acetaldehyde and hydrogen. Senderens believed that these changes were not due to impurities but rather to the method by which the catalysts had been prepared.

Shortly after the discovery of calcium carbide, de Forcrand attempted to prepare calcium ethylate by the reaction of cal-

<sup>70</sup> Ber., 34, 3586, (1901).

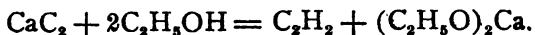
<sup>71</sup> Sabatier and Senderens, Compt. Rend., 136, 738, (1903).

<sup>72</sup> Senderens, Compt. Rend., 144, 381, (1907).

<sup>73</sup> Senderens, Compt. Rend., 144, 1109, (1907).

<sup>74</sup> Senderens, Compt. Rend., 146, 125, (1908).

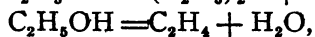
cium carbide and ethyl alcohol, according to the following equation:



For this purpose he heated absolute alcohol with calcium carbide in a sealed tube at  $180^\circ$  for many hours, at the end of which time the walls of the tube were covered with a white crystalline substance, which soon changed into an amorphous powder, when pressed out upon a porous plate. Forcrand found two different alcoholates,  $(\text{CaO})_3(\text{C}_2\text{H}_5\text{OH})_4$  and  $(\text{CaO})(\text{C}_2\text{H}_5\text{OH})$ , but no calcium ethylate. The alcoholates always contained a slightly greater amount of alcohol than that required by the formulas which he assigned to them. They readily absorbed carbon dioxide from the air.<sup>75</sup>

Lefebvre's experiments have already been mentioned. At  $500^\circ$  he found that calcium carbide reacted with alcohol to form a mixture of gases and some aldehyde.<sup>76</sup>

Alcohol reacts in the presence of catalytic agents at high temperatures in three different ways, which can be expressed by simple equations, but the reactions are frequently more complex because certain of the products are capable of undergoing further reaction and the final result in most cases is a very complex mixture of products. The three simple reactions are the following and the extent to which any of them will run depends upon the catalyst, the temperature, and the velocity of the vapor.



### THE REACTION OF ETHYL ALCOHOL AND CALCIUM CARBIDE.

For some time we have been accustomed to dehydrate ethyl alcohol by allowing it to stand over powdered calcium carbide in a flask, closed by a calcium chloride tube, We have fre-

<sup>75</sup> de Forcrand, *Compt. Rend.*, 119, 1266, (1894).

quently noted an evolution of acetylene several weeks after the calcium carbide and alcohol had been placed the flask.

It seemed as if the water must have been removed from the alcohol and that the formation of acetylene was due to some other cause.

Alcohol was heated to boiling under a reflux condenser, with calcium oxide for two days, and a half liter of the distillate was poured into a round-bottomed flask which contained 100 grams of finely powdered calcium carbide. A reaction started at once and produced so much heat that the alcohol began to boil, and it was necessary to attach the flask to a reflux condenser, under which the contents of the flask were allowed to boil for a day. The clear liquid was poured off and on distillation was found to be unchanged alcohol. The residue of carbide in the flask was placed in a copper retort and distilled; the careful fractionation of this liquid yielded two or three cubic centimeters of a high boiling liquid. In a second experiment with the same quantities of reagents only a very slight heating effect was noted, but after boiling the alcohol for three days under a reflux condenser it turned a pale yellow color and crystals were deposited upon the walls of the flask. Since every attempt to filter the hot alcoholic solution failed because of its great viscosity, the clear liquid was poured off into several evaporating dishes. In the course of a few minutes the liquid became turbid and after a few hours the contents of the dishes had been transformed into a gelatinous precipitate, which dried upon exposure to the air. This precipitate contained both alcohol and lime. A third experiment was run to ascertain the length of time necessary for the reaction. No heat effect was noted, but after twenty hours the alcohol turned to a color very much like that of the aldehyde resin. This liquid could not be filtered and upon exposure to air deposited a quantity of yellowish white precipitate. This reaction is still under investigation.

A quantity of absolute alcohol, when vaporized over hot calcium carbide in the apparatus already described, formed a

yellow fluorescent distillate, resembling very much in odor and color the distillate obtained from acetaldehyde. Lime and carbon were found in the tube. Usually about 15 per cent of the alcohol was lost in one passage through the furnace and about 10 per cent was converted to a mixture of higher boiling liquids, but no liquid boiling below  $78^{\circ}$  was ever found. At the end of each run the distillate was fractionated and the alcohol was returned to the apparatus, while the higher boiling liquid was saved until a quantity, sufficient for fractionization, was obtained. The gases were collected, and when analyzed were found to have the following composition:

	I.	II.	III.
	Per cent.	Per cent.	Per cent.
CO <sub>2</sub> .....	2.2	1.5	2.6
C <sub>2</sub> H <sub>2</sub> .....	1.4	1.5	1.0
C <sub>2</sub> H <sub>4</sub> .....	6.0	6.0	5.9
CO .....	6.2	6.1	6.1
CH <sub>4</sub> .....	16.4	...	16.8
H <sub>2</sub> .....	59.1	...	55.5

Notable features of the gas are the very small amount of acetylene and the very large amount of hydrogen. This indicates that at the temperature of the experiment acetylene breaks down into carbon and hydrogen. The quantity of carbon monoxide is very much less than that of methane, but the formation of both may be explained by assuming that the alcohol, in part, at least, breaks down into acetaldehyde and hydrogen, and that the aldehyde is the source of the methane and carbon monoxide, but in this case the two gases should be present in equal volumes.

One hundred and thirty-five grams of the high-boiling fraction were submitted to a careful fractionation by means of the Vigreux column, and the result was a series of liquids boiling within the following limits:

I.— $78^{\circ}$ – $81^{\circ}$ , .....	49 grams
II.— $82^{\circ}$ – $85^{\circ}$ , .....	13 grams
III.— $85^{\circ}$ – $105^{\circ}$ , .....	8 grams



IV.—115°-119°.....	36 grams
V.—120°-133°.....	7 grams
VI.—140°-150°.....	10 grams
VII.—150°-170°.....	12 grams

Thus the fraction boiling at 115°-119° comprised about one-half of all the higher boiling compounds because fractions I and II, upon further fractionation, yielded alcohol and a liquid boiling at 110°-119°. Small test portions of the various fractions, when examined with acetyl chloride, reacted quite vigorously and the odor of an ester was noticed. A portion of 15 grams of fraction IV, which boiled at 115°-116°, was placed in a small flask surrounded by ice water, and 18 grams of acetyl chloride were added to it very slowly. Dense clouds of hydrochloric acid gas were given off, some heat was produced, and the liquid turned to a golden brown in color. After a few hours the mixture was warmed to evaporate the excess of acetyl chloride, and the residual liquid was washed with water, to which a small amount of sodium carbonate was added, and was then dried over fused calcium chloride. It distilled at 123°-126°, the boiling point of normal butyl acetate. This distillate was a clear, pleasant-smelling liquid and weighed 19 grams.

The higher boiling fractions, when examined in a similar manner, formed butyl acetate and much smaller quantities of esters having the boiling point of amyl acetate, 145°-150°, and of hexyl acetate, 165°-172°. The higher boiling fractions were mixtures of butyl alcohol with amyl alcohol and hexyl alcohol. Butyl iodide was prepared according to the following method: 15 grams of fraction IV were mixed with 5 grams of red phosphorous in a small flask, connected to a reflux, and 35 grams of iodine were added in small portions during the next hour, and after standing for eight hours the mixture was heated under the reflux condenser for two hours. The reflux was then replaced by a side condenser, and the distillate, colored a deep brown by the free iodine, was well shaken up with a dilute solution of sodium hydroxide, and, when colorless, was washed with water and dried over fused calcium

chloride. Twenty-four grams of butyl iodide, boiling at  $131^{\circ}$ , were obtained.

In the last experiments with alcohol, the gas furnace was replaced by a Hoskins multiple unit electric furnace, and experiments are in progress having for their object the increasing of the yield of butyl alcohol. In one experiment the calcium carbide was heated to a glowing red and 71 grams of alcohol were vaporized into the tube. The distillate, weighing 9 grams, was fractionated and 7 grams boiled at  $78^{\circ}$ - $80^{\circ}$ , then the temperature rose to  $95^{\circ}$  and the contents of the flask condensed, with the elimination of water and the formation of a small amount of resin.

The gaseous mixture, formed at bright red heat, had the following composition:

	I.	II.
	Per cent.	Per cent.
CO <sub>2</sub> .....	1.3	.9
C <sub>2</sub> H <sub>2</sub> .....	.3	.4
C <sub>2</sub> H <sub>4</sub> .....	8.7	7.9
CO .....	22.6	23.0
CH <sub>4</sub> .....	29.2	30.3
H <sub>2</sub> .....	25.2	22.1

This gas consists chiefly of methane, hydrogen, and carbon monoxide, and it contains these gases in almost equal volumes. The decomposition of alcohol at high temperatures is similar to that observed by Jahn, when he passed alcohol vapor over hot zinc. It is probable that the reaction runs in two stages, in the first of which alcohol decomposes into hydrogen and acetaldehyde, and in the second the aldehyde decomposes into methane and carbon monoxide. The concentration of acetylene is very small, but in every analysis a precipitate was formed as soon as the gas was passed into the pipette, filled with ammoniacal silver nitrate. The ethylene results from the decomposition of alcohol into water and ethylene. The concentration of hydrogen is notable, for at lower temperatures hydrogen made up about 60 per cent of the gas.